EXTRACTIVE REACTION OF BIODIESEL SYNTHESIS USING ETHANOL AS A SOLVENT: A CONVERSION STUDY

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ABSTRACT

Worldwide high demand for energy, uncertainty of petroleum resources and concern about global climatic changes has led to the resurgence in the development of alternative liquid fuels. Ethanol has always been considered a better choice as it reduces the dependence on crude oil and promises cleaner combustion leading to a healthier environment. Developing ethanol as fuel beyond its current role of fuel oxygenate, would require lignocelluloses as a feedstock because of its renewable nature, abundance and low cost. Nevertheless, in most of the studies, methanol was used as the reaction and extraction medium. The use of methanol deviate the purpose of producing renewable energy since methanol is mostly derived from fossil fuel. Therefore in this study, the use of ethanol as the extraction and reaction medium for biodiesel synthesis to produces FAEE was investigated. The objective of this research is to determine the effect varying extraction rate on the biodiesel production by extractive reaction from palm oil using ethanol as a solvent. The experimental procedure to produce biodiesel consist of 2 major experiment which were control experiment and extractive reaction experiment. Operating condition is at 60 ˚C of temperature with molar ratio of ethanol to oil is 6:1 was fixed. The study shows, the extractive rate on the conversion of ethanol in biodiesel synthesis was improved by the extraction system. As a conclusion, ethanol have a better oil extraction property by applying the extractive reaction.

Keywords: Extractive Reaction, Biodiesel, Ethanol as a solvent, Free Fatty Acid Ethyl Ester (FAEE)

ABSTRAK

Permintaan yang tinggi di seluruh dunia untuk sumber tenaga adalah semakin memberangsangkan, tetapi kekurangan sumber petroleum dan kebimbangan mengenai perubahan iklim global telah membawa kepada kebangkitan semula dalam pembangunan bahan api cecair alternatif. Etanol telah dianggap sebagai pilihan yang lebih baik kerana ia mengurangkan pergantungan kepada bahan api mentah, menjanjikan pembakaran yang bersih dan membawa kepada persekitaran yang lebih sihat. Mengolah etanol sebagai bahan api di luar peranannya yang sebenar sebagai bahan api oksigen adalah langkah yang bijak kerana etanol boleh terhasil daripada kanji yang boleh didapati dari alam semula jadi. Ia adalah bahan mentah yang boleh diperbaharui, dan kos penghasilan yang rendah. Namun begitu, dalam kebanyakan kajian, metanol telah digunakan sebagai bahan tindak balas dan medium pengekstrakan. Penggunaan metanol menyimpang tujuan menghasilkan tenaga yang boleh diperbaharui oleh kerana metanol kebanyakannya berasal daripada bahan api fosil. Kajian ini dibuat, khusus kepada penggunaan etanol sebagai pengekstrakan dan medium tindak balas untuk menghasilkan biodiesel. Objektif kajian ini adalah untuk menentukan kesan pengekstrakan pada kadar yang berbeza untuk pengeluaran biodiesel oleh tindak balas ekstraktif daripada minyak sawit menggunakan etanol sebagai bahan pelarut. Langkah-langkah kajian untuk menghasilkan biodiesel terdiri daripada dua kajian utama, yang pertama ialah eksperimen kawalan dan yang kedua eksperimen tindak balas ekstraktif. Tindak balas kajian beroperasi pada suhu 60˚C dengan nisbah molar etanol kepada minyak 6:1 telah ditetapkan. Kajian menunjukkan, kadar ekstraktif pada penukaran etanol dalam sintesis biodiesel telah bertambah kepada lebih baik oleh sistem pengekstrakan. Sebagai kesimpulan, etanol mempunyai perahan minyak yang lebih baik dengan menggunakan tindak balas ekstraktif.

Kata Kunci: Tindak balas ekstraktif, Biodiesel, Ethanol sebagai pelarut, Asid Lemak Ethyl Ester (FAEE)

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%	Percentage
FAEE	Fatty Acid Ethyl Ester
CH_4OH	Ethanol
Al_2O_3	Aluminium Oxide
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
DMAP	Dimethylaminopyridine
FFA	Free Fatty Acid
TG	Triglyceride
GC	Gas Chromatography
GC-FID	Gas Chromatography-Flame Ionized Detector
DRF	Detector Response Factor
˚ C	Degree Celsius

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Currently, biodiesel has received attention, as petroleum prices and concern for the environment have increased. Biodiesel can be used with little or no modifications to existing diesel engines, and has a low emissions profile (BiodieselNow, 2006). Biodiesel has lower emissions than regular diesel and does not contribute to an increase in carbon dioxide in the atmosphere since all the material comes from plants, and extends the life of the engine due to its good lubricity. Biodiesel is a renewable fuel derived from vegetable oils and animal fats that can be used in diesel engines. Though biodiesel reduces hazardous emissions, other environmental factors such as land cultivation and competition with agricultural products for human consumption make biodiesel more of a short term alternative energy.

The possibility of using vegetable oils as fuel has been recognized since the beginning of Diesel engines. Vegetable oil has too high a viscosity for use in most existing Diesel engines as a straight replacement fuel oil. There are a number of ways to reduce the viscosity of the vegetable oil. Dilution, micro-emulsification, pyrolysis and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. One of the most

common methods used to reduce oil viscosity in the biodiesel industry is called transesterification. Chemical conversion of the oil to its corresponding fatty ester is called transesterification. (Bala, 2005). **Figure 1** shows the transesterification reaction of triglicerides.

$3C_2H_5OH$ + Triglyceride ↔ 3FAEE + Glycerol
(Ethanol) (Fatty Acid Ethyl Ester)

Figure 1.0: Transesterification of triglyceride with alcohol to form biodiesel

One popular process for producing biodiesel from the fats/oils is transesterification of triglyceride by methanol (methanolysis) to make methyl esters of the straight chain fatty acid. However, this makes the biodiesel produced not 100% renewable since methanol is a fossil-fuel base product. Besides, ethanol which was reported to have better oil extraction solvent due to its longer alkyl chain and less polarity as compared to methanol in which the non-polar oil will be more easily dissolved so ethanol is good to overcome the limiting factor in reactive extraction process (Lee C.G, 2000).

The biodiesel reaction requires a catalyst such as potassium hydroxide (KOH)/ sodium hydroxide (NaOH) to split the oil molecules and an alcohol (methanol or ethanol) to combine with the separated esters. The main byproduct is glycerin. The process reduces the viscosity of the end product. Transesterification is widely used to reduce vegetable oil viscosity (Pinto AC, 2005).

1.2 Problem Statement

The biodiesel synthesis involves multiphase that may render mass transfer effects to be significant. Extraction is one of the potential methods in separating reactors that can be used to improve the reaction yield. In particular, a liquid-liquid system of extraction is favorable due to the low temperatures window of the transesterification reactor of edible or non-edible oil with short chain alcohols such as ethanol and methanol. The liquid-liquid extraction is a controlled mass transfer operation in which a liquid solution (the feed) is contacted with an immiscible or nearly immiscible liquid. Biodiesel production in Malaysia is apparently practical to the use of non-edible oils and palm oil as the feedstock. Biodiesel that is available in the market is currently produced using methanol as the source of alcohol. However, this makes the biodiesel produced not 100% renewable since methanol is a fossil-fuel base product. Moreover, using methanol as alcohol source in biodiesel production will lead to uncertainty in product cost and supply since fossil sources in the world are now depleting (Gui M.M., Lee K.T. and Bhatia S;, 2009). Therefore, using ethanol which can be derived from renewable sources such as lignocelluloses material as alcohol source would be a potential solution to overcome this limitation. Besides, ethanol which was reported to have better oil extraction property (Lee C.G., 2000) is additionally expected to be able to overcome the limiting factor in reactive extraction process by means of simultaneously-continuous extraction (Shuit S.H., 2010). When ethanol is employed, fatty acid ethyl esters (FAEE) will be obtained as the products of the transesterification reaction while the alcohol extracting the product from the oil phase where the reaction occurs. Thus the aim of this study is to study the phenomena of extractive reaction using ethanol as alcohol source for the production of biodiesel from palm oil (Venice, 2010).

1.3 Objective

The purpose of this thesis is:

- To determine the effect varying extraction rate on the biodiesel by including proper rate of reactant and solvent.

- To characterizes and assess the efficiency of using ethanol as a solvent.

1.4 Scope of the research work

In order to achieve the target, extra effort and focus have to be done with the topic of extractive reaction of biodiesel synthesis using ethanol as a solvent

- The reaction temperature is between 60°C-70°C
- The identification components of oil and ethanol is analyze by Gas Chromatography

1.5 Rationale & Significance of Study

This studies was been carried out to synthesize and develop the phenomena of extractive reaction using ethanol as alcohol source for the production of biodiesel from palm oil:

- Triglyceride source is palm oil : readily available vegetable oil in Malaysia
- New technique in producing biodiesel with less unit operations and heat loss.
- Analyze the small-scale reactions to serve as a model for industrial production.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The biodiesel is a mixture of methyl or ethyl esters of fatty acids that can be used as a fuel for diesel engines. The ester group increases the oxygen content of diesel-biodiesel blends improving the efficiency of the combustion of the conventional fossil diesel. For producing biodiesel, the transesterification of vegetable oils with low molecular weight alcohols like methanol or ethanol is necessary. This reaction is accomplished with the help of acid, basic or enzymatic catalysts. Usually, biodiesel production in the world is carried out employing methanol and basic catalysts (mostly KOH). The most employed vegetable oils are rapeseed, soybean and sunflower oils. The oil from palm (*Elaeis guineensis*) is considered as an excellent feedstock for biodiesel production in tropical countries. The conventional technologies for biodiesel production employ reactors with acid or basic catalysts and a separation scheme that uses unit operations like distillation, centrifugation, flash evaporation, filtration, and decantation. The purification of this biofuel through the operation mentioned implies high capital investment and energy consumption leading to elevated production costs. Process design trends in chemical industry are related to the development of more efficient technologies. One of the most important approaches for the design of

more intensive and cost-effective process configurations is process integration, which looks for the integration of all operations involved in the production of one specific product. This can be achieved through the development of integrated processes that combine different steps into one single unit. The reactive extraction is an integrated process simultaneously combining the chemical reaction and liquid-liquid extraction. The latter phenomenon allows the continuous removal of the reaction products favouring the direct conversion in the case of reversible reactions like the esterification of vegetable oils with methanol. The objective of this work is to evaluate the possibility of applying the integration principle to the biodiesel production from palm oil by extractive reaction. (Gutiérrez L. F, 2010)

2.2 Catalyst

Catalyst is a substance for change in rate of a chemical reaction. A catalyst may participate in multiple chemical transformations. Promoter is a substance that increasing the reactivity of catalyst while catalytic poisons is a substance that deactivated catalyst. Catalyst divided by heterogeneous catalyst and homogeneous catalyst. Heterogeneous catalysts such as Palladium on activate charcoal used in the reaction of hydrogen with nitro groups to produce amine groups. Homogeneous catalyst such as DMAP (dimethylaminopyridine) used in solution to catalyst esterification reactions.

2.3 Homogeneous Catalyst

(G. Vicente et al., 2003) studied a comparison of different homogeneous catalyst system (Integrated biodiesel production). A comparison is made of different basic catalyst which is sodium methoxide, potassium methoxide, sodium

hydroxide and potassium hydroxide for methanolysis of sunflower oil. In their findings, the methyl ester concentrations were near 100wt% when used four catalysts. For the methoxide catalysts, biodiesel yields were higher than 98wt% after the separation and purification step while biodiesel yields for sodium and potassium hydroxide were lower namely 85.9 and 91.67 wt%. The biodiesel yields can be higher when a modification of the value for experimental conditions such as temperature and catalyst concentration.

(D. A. G. Aranda et al., 2007) studied the acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. In this experiment, used different of homogeneous catalyst such as sulfuric acid, methanesulfonic acid, phosphoric acids were the best catalysts. In their findings, sulfuric and methanesulforic acids were the best catalyst, with conversion higher than 90% at 1 h of reaction for reactant methanol and ethanol. For different alcohols, methanol reaction was faster than ethanol. For effect of water in the reaction medium, inhibition effect can be found in the ethanol reaction. A small amount of catalyst (0.01 w/w) is enough to promote the reaction.

(T. Joseph et al., 2005) studied a green, efficient and reusable catalyst system and reaction medium for Fischer esterification by bronsted acidic ionic liquids. Bronsted acidic ionic liquid containing nitrogen based organic cation 1-methylimidazole and 1-buthyl-3-methylimidazolium and inorganic anions of the type BF4, PF6 and PTSA. In their findings, a maximum 100% conversion and 100% product selectivity was obtained on using PTSA as catalyst over a period of 2 h. For PF6 used in the reaction also gave 100% conversion in 2 h but only 90% selectivity for ester was achieved. In the effect of mole ratio of imidazole and BF4 that on increasing the amount of anion in the ionic liquid, the conversion increases but the selectivity remains the same. The reaction had to be carried out for longer

time for complete conversion. When the temperature was increase to 120°C, the conversions also increase.

(B. Tosh et al., 2000) studied the homogeneous esterification of cellulose in the lithium chloride-N, N-dimethylacetamide solvent system: effect of temperature and catalyst. In their findings, LiCL-DMAc was found to be an excellent solvent system for the acetylation of cellulose with acetic anhydride in the presence of p-TsCL or pyridine. Pyridine is more active as a catalyst for esterification than p-TsCL. In case of esterification with higher anhydrides, p-TsCL might serve as a better catalyst.

(M. Di Serio et al., 2005) studied the synthesis of biodiesel via homogeneous Lewis acid catalyst. In their finding, bivalent cations are catalyst for both transesterification and esterification reactions. Catalytic activities are related to the Lewis acid strength of the metals and to the molecular structure of the anion a complex. The best catalytic performances were obtained with cation metals having stability constant with dibenzoilmetane in the range between 8.60 (corresponding to cadium) and 10.23 (corresponding to zinc). Then, the stearates have better performances than acetates.

2.4 Heterogeneous Catalyst

Heterogeneous catalyst was present in a different phase, usually in solid phase. Heterogeneous catalyst has many advantages that main advantage is the relative ease of catalyst separation from the product stream that aids in the creation of continuous chemical processes. Heterogeneous catalyst was typically

more tolerance of extreme operation condition. It is to be select for this experiment.

(J.M. Marchetti et al., 2006) studied the heterogeneous esterification of oil with high amount of free fatty acids. In their experiment, basic resin was use as a heterogeneous catalyst. In their findings, the final conversion follows an endothermic behavior when temperature is changes. Resin should be added during the process at initial FFA amounts changes to increase the final conversion. On the amount catalyst, when more catalyst is added a little higher reaction rate is achieved. In the resin is reused, the final conversion is achieved for 2nd, 3rd, and 4th reuse was less than 25%. They conclude that the resin should to be regenerated after each process and resins are a heterogeneous catalyst is appropriate to perform the esterification with higher conversion.

(H. Joo Kim et al., 2004) studied the transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. In their experiment, Na/NaOH/γ-Al_2O_3 is use for heterogeneous base catalyst. In their finding, the activities of the heterogenous base catalysts correlated with their basic strengths. *n*-hexane was the most effective with a loading amount of 5:1 VO to *n*-hexane molar ratio when the co-solvent tested. The ratio optimum methanol to oil loading was found to be 9:1. For different catalyst, the Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst showed almost the same activity under optimized reaction condition compared to the homogeneous NaOH catalyst.

(F. T. Sejidov et al., 2005) studied the esterification reaction using solid heterogenous acid catalyst under solvent-less condition. In their finding, esterification reaction of phthalic anhydride by 2-ethylexanol in the presence of solid acidic catalyst have been investigated under solvent-less condition. For the

best reactivity and efficiency among the investigated heterogenous catalyst is sulfated zirconia. These catalysts are environmentally friendly and cleaner than homogeneous catalyst.

(Y. Moo Park et al., 2008) studied the heterogenous catalyst system for the continuous conversion of free fatty acid in used vegetable oils for the production of biodiesel. In their finding, the SO_4/ZrO_2 and WO_3/ZrO_2 catalysts were found to be effective in the esterification of free fatty acid to FAME. When the properties of the catalyst are different, it is difficult to compare batch reaction with packed-bed reactions. Packed-bed reactions have advantages over batch reactions in terms of mass production but have some disadvantages when their activity is considered. For maximize the activity of the catalyst, the optimization of the catalyst pellet size will be needed. For the characterization, the oxidation state of W is mainly related to the catalytic activity of WO_3/ZrO_2.

Table 2.1: Summary for the Homogeneous Catalyst

Author	Reaction	Catalyst	Finding
G. Vicente et al., (2003)	Esterification (Biodiesel production from sunflower oil)	Sodium Methoxide, Potassium Methoxide, Sodium Hydroxide and Potassium Hydroxide	Biodisel yields were higher when used Methoxide catalyst.
D. A. G. Aranda et al., (2007)	Esterification (Biodiesel production from Palm Fatty Acid)	Sulfuric Acid, Methanesulfonic Acid, phosphoric Acid and Trichloroacetic	Sulfuric and Methanesulfonic Acids were the best catalyst.

		Acid	
T. Joseph et al., (2005)	Esterification (Acetic acid with Benzyl Alcohol)	Bronsted Acidic ionic liquid (BF4, PF6 and PTSA)	PTSA is the best catalyst than BF4 and PF6.
B. Tosh et al., (2000)	Esterification (Cellulose in the lithium chloride–*N*,*N*-dimethylacetamide solvent system)	*p*-TsCL and Pyridine	Pyridine is more active as a catalyst for esterification than *p*-TsCL.
M. Di Serio et al., (2005)	Transesterification and Esterification (Triglycerides (TG) with Methanol)	Lewis Acid catalyst	The best catalytic performances were obtained with cation metals having stability constant.

Table2.2: Summary for Heterogeneous Catalyst

Author	**Reaction**	**Catalyst**	**Finding**
J. M. Marchetti et al., (2006)	Esterification (Oil with high amount of free fatty acids)	Basic resin	The basic resin is the best catalyst for esterification reaction.
H. Joo Kim et al., (2004)	Transesterification (Vegetable oil to biodiesel using heterogenous base catalyst)	Na/NaOH/γ-Al_2O_3	Na/NaOH/γ-Al_2O_3 heterogenous base catalyst showed almost the same activity.

F. T. Sejidov et al., (2005)	Esterification (Phthalic Anhydride by 2-Ethylhexanol)	Sulfated Zirconia	Sulfated Zirconia is the best reactivity and efficiency.
Y. Moo Park et al., (2008)	Esterification (Oleic Acid with Methanol)	SO_4/ZrO_2 and WO_3/ZrO_2	The SO_4/ZrO_2 and WO_3/ZrO_2 catalysts were found to be affective in the esterification of free fatty acid to FAME

2.5 Biodiesel Production

Main feedstock for biodiesel production analyzed in this work is palm oil that is a mixture of triglycerides. The overall process for biodiesel production comprises the following steps: feedstock conditioning, reaction, separation, and product purification. During feedstock conditioning, the content of water and free fatty acids in the vegetable oil should be controlled in order to avoid undesirable reactions and products (soap). Thus, the conditioning strongly depends on the extraction method of the vegetable oil and on its origin. The reaction step includes the transesterification reaction between the triglycerides of the oil and low molecular weight alcohols (methanol or ethanol) in the presence of a catalyst (homogeneous or heterogeneous) to form fatty esters (biodiesel) and glycerol.

The transesterification comprises three successive reversible reactions in which each one of the fatty acids linked to glycerol are to be esterified. The first step is the conversion of the triglycerides into diglycerides followed by the conversion of the diglycerides into monoglycerides and, finally, the conversion of the monoglycerides into glycerol producing one molecule of the ester per each glyceride in each step. The main products are the esters of the fatty acids

(biodiesel) and glycerol. Due to the reversible character of this reaction, an excess of alcohol is employed to increase to a decanter where two liquid phases are separated: biodiesel-enriched and glycerol-enriched phases. In general, for acid and alkaline processes, neutralization of the catalyst in each phase is needed after biodiesel separation in order to form salts that could be removed afterwards. After neutralization, the biodiesel phase undergoes washing with hot water to remove the salts and the non-separated glycerol. The glycerol is dried by distillation or flashing. If economically viable, the glycerol is refined to obtain a valuable co-product.

The application of extractive reaction is one of the integration approaches that can be utilized for the intensification of biodiesel production. This process consists in the combination of the chemical reaction and liquid-liquid extraction in the same unit achieving such synergistic effect, that the increase of selectivity, conversion, productivity, and purity of final product may be attained (Rivera and Cardona, 2004). Thus, two liquid phases are formed during the reaction. In this way, the principle of reaction-separation integration can be applied to the production of ethyl esters using palm oil and even castor oil. Biodiesel-enriched liquid phase is removed from the reactor-extractor and sent to a flash unit where ethanol is recovered. In order to obtain a high purity biodiesel, this stream is washed with hot water to extract the excess of NaOH or KOH and the soap that could have been formed during the reaction. Glycerol-enriched phase is directed to another flash unit where part of ethanol is recovered. If high purity glycerol is to be obtained, a distillation column working under vacuum conditions (0.2 atm) is required (Gutiérrez et al., 2009).

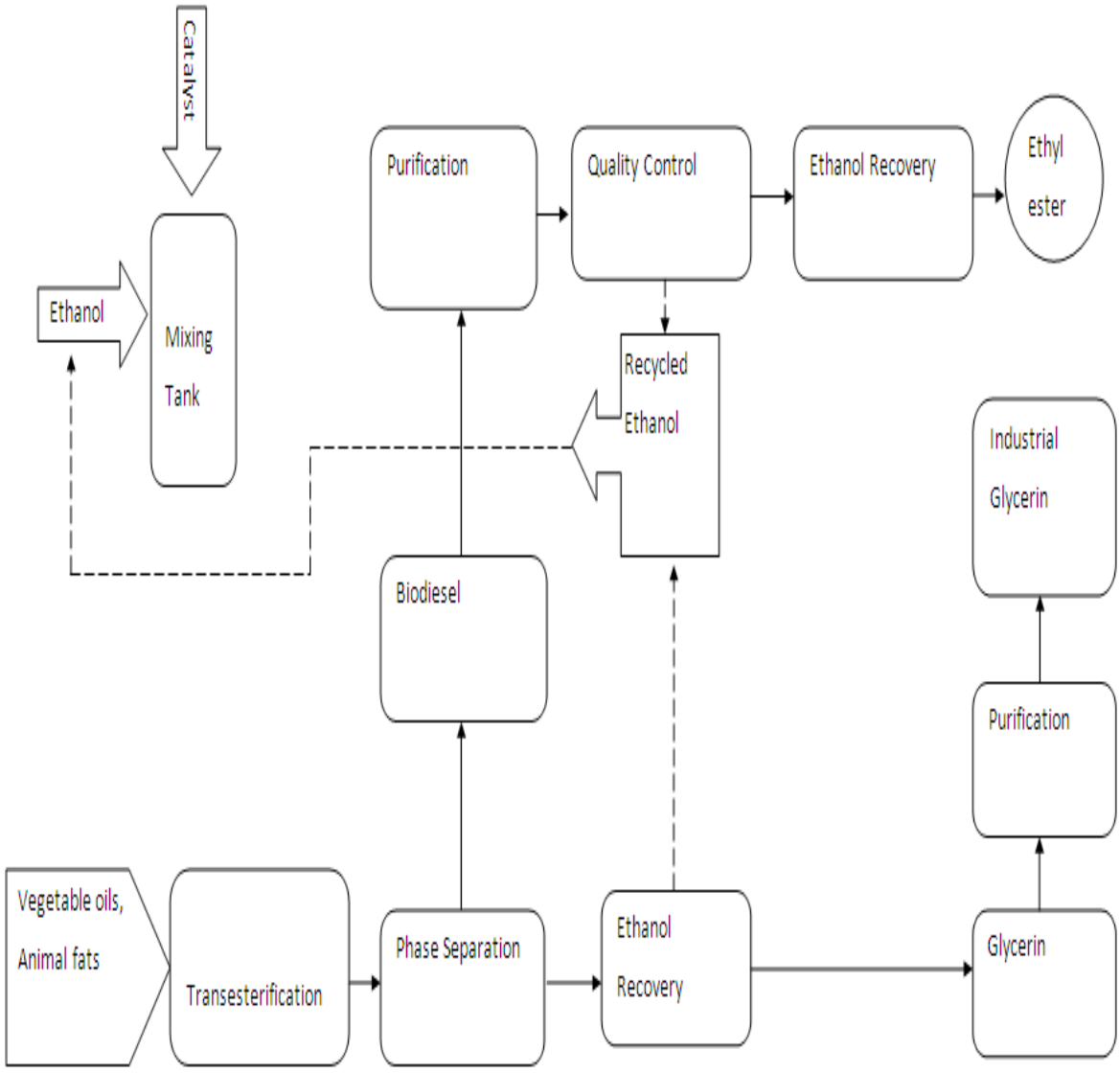

Figure 2.1: Main Step of Biodiesel Production

CHAPTER 3

METHODOLOGY

3.1 Introduction

In order to produce biodiesel, five major steps involved. These steps the equipment selection, raw material preparation, experimental procedure, sample preparation for GC analysis and analytical method. In the experimental at procedure, the reaction was conducted using heterogeneous catalyst, potassium hydroxide (KOH). In this experiment, the molar ratio of ethanol to palm oil was fixed at 6:1 ratios and the reaction temperature at 60˚C. To analyze the biodiesel product, gas chromatography was used. The flow process of the experiment was illustrated and discuss in the subtopics below. The general flow of the experiment was illustrated in the figure below.

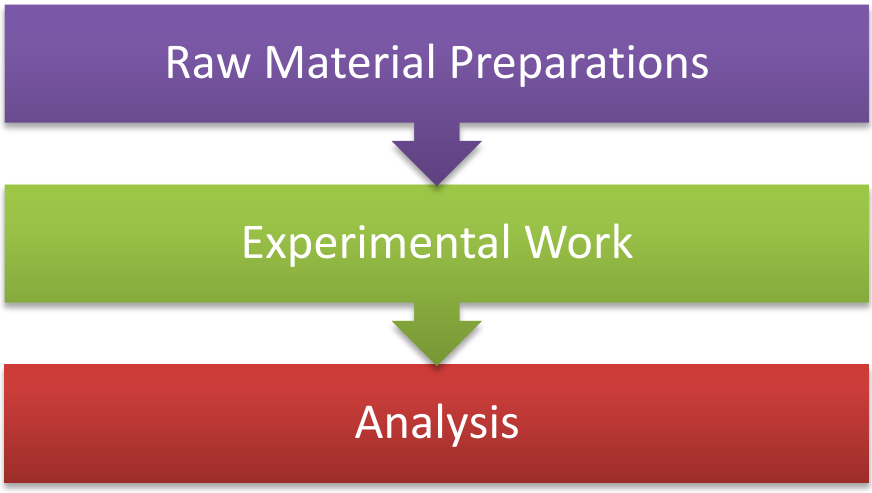

Figure 3.1: Main Methodology Flow Chart